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NMR Studies of Polymeric Solid Electrolytes

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A complete list of publications emanating from work performed under the grant is given. This is followed by summaries of the principal findings quoted in previous reports and some new research directions evolving from these findings. A list of students and post doctorals involved in the research is also given.

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List of Journal Articles Emanating from Contract

1. "Ionic and Molecular Motion in a Superionic Sodium Poly(ethylene Oxide) Complex", Solid State Ionics 15, 259 (1985).

2. "Electrically Conducting Poly(vinyl acetate)", with M.C. Wintersgill, J.J. Fontanella, J.P. Calame, C.G. Andeen, J. Electrochem. Soc. 131, 2208 (1984).

3. "NMR, Electrical Relaxation and High Pressure Conductivity in Ion Conducting Polymers", with J.J. Fontanella, in Relaxations in Complex Systems, K.L. Ngai, G.B. Wright, eds., Office of Naval Research, 1985, p. 211.

4. "Conductivity, DSC, FTIR and NMR Study of Poly(vinyl acetate) Complexed with Alkali Metal Salts", with M.C. Wintersgill, J.J. Fontanella, J.P. Calame, M.K. Smith, T.H. Jones, K.J. Adamic, A.N. Shetty, C.G. Andeen, Solid State Ionics 18&19, 326 (1985).

5. "Ionic Conductivity in Solid, Crosslinked Dimethylsiloxane-Ethylene Oxide Copolymers Networks Containing Sodium", with K.J. Adamic, M.C. Wintersgill, J.J. Fontanella, J. Appl. Phys. 60, 1342 (1986).

6. "NMR. DSC, TMA, and High Pressure Electrical Conductivity in Solid, Crosslinked Dimethylsiloxane-Ethylene Oxide Copolymer Networks Containing Sodium", with M.C. Wintersgill, J.J. Fontanella, M.K. Smith, K.J. Adamic, C.G. Andeen, Polymer 28, 633 (1987).

7. "DR, NMR and High Pressure Electrical Conductivity in PPO Complexed with Sodium Perchlorate", with M.C. Wintersgill, J.J. Fontanella, M.K. Smith, Y.S. Pak. C.G. Andeen, J. Electrochem. Soc. 135. 235 (1988).

8. "DSC, Electrical Conductivity, and NMR Studies of Salt Precipitation Effects in PPO Complexes", with M.C. Wintersgill, J.J. Fontanella and K.J. Adamic, British Polymer Journal, 20, 195 (1988).

9. "Amorphous Phase Separation, Salt Precipitation, and High Pressure Effects in PPO Containing NaI", with K.J. Adamic, M.C. Wintersgill, J.J. Fontanella, and C.G. Andeen, in proceedings of the Electrochemical Society Symposium on Electro-Ceramics and Solid State Ionics, 88-3, 211 (1988).

10. "NMR, DSC, and Electrical Conductivity Studies of MEEP Complexed with $NaCF_3SO_3$", with K.J. Adamic, Y.S. Pak, M.C. Wintersgill, and J.J. Fontanella, Solid State Ionics, 28-30, 1042 (1988).

11. "High Pressure Conductivity and NMR Investigation of Siloxane-Based Polymer Electrolytes", with Y.S. Pak, K.J. Adamic, M.C.

Wintersgill, J.J. Fontanella, H.L. Mei, and Y. Okamoto, Molecular Crystals and Liquid Crystals, 160, 347 (1988).

12. "Iodine L-Edge X-Ray Absorption Fine Structure Studies of Polymer - Iodide Salt Complexes", with M.L. denBoer, Molecular Crystals and Liquid Crystals, 160, 339 (1988).

13. "NMR Studies of Na^+ - anion association effects in Polymer Electrolytes", with Y.S. Pak, M.C. Wintersgill, and J.J. Fontanella, Solid State Ionics, 31, 241 (1988).

14. "Electrical Conductivity, Dielectric Relaxation, DSC, and NMR Studies of Amorphous Poly(ethylene oxide) Complexed with Alkali Metal Salts", with A. Al-Mudaris, A.V. Chadwick, D.A. Beam, M.C. Wintersgill, J.J. Fontanella, and C.G. Andeen, Polymer, 30, 1123 (1989).

15. "^{13}C NMR Studies of Poly(propylene oxide) Complexed With Alkali Iodides", with R.E. Stark and Y.S. Pak, Solid State Ionics, 34, 275 (1989).

16. "Polymer Electrolytes with Exclusive Cationic Conductivity", with H. Liu, Y. Okamoto, Y.S. Pak, K.J. Adamic, Materials Research Society Symposium on Solid State Ionics, 1988, 135, 343 (1989).

17. "Dielectric Relaxation Studies of Polymer Electrolytes", with J.J. Wilson, M.C. Wintersgill and J.J. Fontanella, Elsevier Applied Science Series, in press.

18. "ESR Studies of Divalent Copper in Polymer Electrolytes", with K.J. Adamic, F.J. Owens, M.C. Wintersgill and J.J. Fontanella, Elsevier Dielectric Relaxation M.L. denBoer, K.J. Adamic, M.C. Wintersgill and J.J. Fontanella, Physical Review B, submitted.

19. "Electric Modulus and Multi-frequency ^{23}Na NMR Study of Poly(propylene oxide) Complexed with Sodium tetraphenylborate", with M.C. Wintersgill, J.J. Fontanella, Y.S. Pak, K.J. Adamic, submitted to Solid State Ionics.

Technical reports for all of the above papers, except for #19, have been submitted. A summary of significant results emanating from the contract, condensed from previous Year-End Reports, appears below.

Sodium 23 Sodium (+)

A wide variety of polymer electrolytes containing mobile Na^+ ions have been studied by ^{23}Na NMR. Much of this work has been in collaboration with Profs. J. Fontanella and M. Wintersgill at the US Naval Academy, who provided complex impedance and thermal measurements complementary to the NMR. Certain behavior, for example motional averaging of the NMR linewidth above T_g and subsequent lifetime broadening about 60K above T_g was found to be common to all polymer hosts studied, including cross-linked PEO,

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PPO, MEEP and siloxane-PEO copolymers. Other highlights include the synthesis (by collaborator Prof. Y. Okamoto of Polytechnic University) and study of single ion (cation) conductors, the development of high-pressure (up to 2.5 kbar) NMR capability, and the use of ESR to study ionic motion in Cu^{2+}- containing polymer electrolytes. Under the momentum of 6 years of ONR funding, we have established a number of contacts with other scientists interested in polymer electrolytes. Among these are: T. Skotheim, Brookhaven Labs (joint publications); K. Abraham, EIC Labs (joint investigations in progress); B. Scrosati, University of Rome (I will spend the first part of my sabbatical leave there). In addition, our expertise developed under ONR funding has led to a small contract from NSWC (Bill Kilroy, contract monitor) to study Li ion conductors in conjunction with their Li-thionyl chloride battery program. We have now developed a program (unfunded) to extend our measurements to include ^7Li NMR.

Although the deuteron NMR work (in collaboration with Prof. U. Stimming, Columbia University) described in my 1989 Year-End Report has not yet resulted in any publications, it did provide valuable guidance in determining the phase diagram in frozen aqueous KOH solutions. An interesting spin-off of this work has been our recently published study of deuteron NMR in polyimide films containing water (unfunded).

A number of undergraduate and graduate students have been involved in the above work, they are listed below:

1. Robert Feiertag, M.A., 1985, presently at Computer Sciences Corp., Maryland.

2. Gillian Reynolds, M.A., 1988, presently in the Physics Ph.D. program at M.I.T., and recipient of NIH Minority Access Predoctoral Fellowship.

3. Meng Chiao, B.A. 1988, presently in the Physics Ph.D. program at UCLA.

4. Armando Howard, B.A., 1990, will begin graduate study in astrophysics at Princeton in the Fall of 1990, has been offered both NSF and AT&T Minority Predoctoral Fellowships.

5. Yiu Sun Pak, Ph.D. 1990, will defend thesis in May 1990.

6. Shizhe Li, Ph.D. expected late 1991.

7. Sandra Brown, undergraduate Minority Access Scholar.

In addition, one postdoctoral associate, Dr. Kresimir Adamic, has received partial support during the term of the Contract.